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THE TITANIUM-ALUMINUM PHASE DIAGRAM - A REVIEW OF THE NEAR Ti-50 At.% Al PHASE FIELDS

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ABSTRACT

The understanding of the titanium-aluminum (Ti-Al) phase diagram is of great importance to the development of titanium-aluminide alloys and composites for high temperature applications. In this report, the Ti-Al phase diagram near 50 atomic percent (at.%) aluminum is critically reviewed. Murray's Ti-Al phase diagram has been well accepted by the materials community in the late 1980s. Recent results from solidification experiments point toward the existence of a high temperature α phase field consistent with two high temperature peritectic reactions ($\beta + L \rightarrow \alpha + L \rightarrow \gamma$) near 50 at.% aluminum. These reactions are not accounted for in Murray's Ti-Al phase diagram. Close evaluation of the past experimental techniques by which data were utilized in Murray's calculation of the Ti-Al phase diagram revealed areas of uncertainties. These uncertainties are primarily due to the limitation of analytical capabilities available at the time the experiments were performed.

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CONTENTS

INTRODUCTION

Titanium Aluminides at a Glance

Fueled by material requirements under the DoD (Department of Defense) industrial Integrated High Performance Turbine Engine Technology Initiative (IHPTET), NASA High Temperature Engine Materials Technology Program (HITEMP), and the development of the National Aerospace Plane (NASP), intermetallics are undergoing intense research and development aimed at exploiting their high temperature capabilities. In particular, titanium-aluminide and titanium-aluminide composites have demonstrated attractive high temperature properties and are the focus of numerous past and present research efforts.[1]

At high temperature, titanium-aluminides exhibit excellent characteristics as engine materials for a number of reasons. High temperature stiffness retention is attributed to strong atomic titanium-aluminum (Ti-Al) bonds. Titanium-aluminides also have high activation energy for self diffusion. Since creep mechanisms are associated with diffusion, excellent creep resistance is exhibited in titanium-aluminides. Another advantage with titanium-aluminides is the availability of aluminum atoms for oxidation on the surface. Continuous supply of aluminum atoms is required for alumina formation as oxide layers spall off during thermal cycling. Alumina is the stable oxide on titanium-aluminide and it provides excellent alloy protection in high temperature oxidizing environment. These and other properties of titanium-aluminides have prompted enormous interest from aerospace industries. Major obstacles to the board utilization of titanium-aluminides for engine and structural applications are their poor room temperature properties. Low ductility and low fracture toughness at ambient temperature are some of the major problems currently being addressed.[2] Furthermore, research studies have raised the concern for hydrogen embrittlement in titanium-aluminides.[3,4] Significant progress in improving ambient temperature ductility and fracture toughness is made through alloying and thermomechanical processing.[5] Several engine producers are currently evaluating titanium-aluminide alloys for a variety of components.

Titanium-aluminide research today mainly focusses on alpha 2 ($\alpha 2$) base alloys and gamma (γ) base alloys. The $\alpha 2$ phase, Ti_3Al, has an ordered hexagonal (DO_{19}) crystal structure whereas the γ phase, Ti-Al, has an ordered face-centered tetragonal ($L1_0$) crystal structure. The majority of $\alpha 2$ alloys and γ alloys studied have a dual phase microstructure for the best combination of properties. The dual phase $\alpha 2$ alloys are generally composed of $\alpha 2$ and β-Ti (bcc) phases. The β phase occurs as either ordered (B2) or disordered (bcc) phase depending upon the alloying content. The dual phase γ alloys are composed of γ and $\alpha 2$ phases. While $\alpha 2$ alloys exhibit good room temperature ductility and toughness, γ alloys have better strength retention at a higher temperature. More recently, an orthorhombic titanium-aluminide based on Ti_2AlNb, known as the O-phase, reported higher temperature strength retention and better room temperature ductility than most $\alpha 2$ alloys and γ alloys.[6]

Significant attention is also being given to the study of intermetallic composites. Intermetallic composites are identified by their reinforcement types. Reinforcements consist of continuous fibers, discontinuous fibers, particulates, and whiskers. Each class of intermetallic composites has its own *pros and cons* regarding processing, properties, and cost. Continuous fiber reinforced intermetallic composites provide excellent high temperature stiffness and strength with good damage tolerance. Textron's Specialty Material Division of Lowell, MA is the prime producer of silicon carbide fiber reinforced intermetallics. The question to be answered prior to utilization of continuous fiber reinforced intermetallics is whether good damage tolerance will satisfy engineering applications with fracture toughness requirements.

In the area of dispersion intermetallic composite, one of the most promising materials is Martin Marietta's XD™ Titanium Aluminide.[7] Rather than blending or mixing from a second phase, the reinforcements in XD™ Titanium Aluminide composites are formed via an *in situ* solution-reprecipitation process.[8,9] The dispersoids are precipitated from an exothermic reaction in the melt. XD™ composites of TiB_2 particulate reinforced $\gamma/\alpha 2$ exhibited promising room temperature ductility and toughness.[10] In the XD™ intermetallic composites, the dispersoids act as nucleation sites in refining the as-cast microstructure. A fine microstructure in intermetallics provides good room temperature ductility. At anticipated operating temperature, the reinforcements pin grain boundaries in retarding creep flow thus retaining excellent mechanical properties. Recent studies at the U.S. Army Materials Technology Laboratory (MTL) also showed interesting dynamic behavior of the XD™ Titanium Aluminide impacted with a tungsten long rod penetrator.[11]

In addition to alloying and innovative composites design, secondary processing such as heat treatments and thermomechanical deformation are means by which a wide range of microstructures are attained. The resulting material properties are greatly dependent on and are sensitive to the microstructure.[12] In all of the aforementioned processing methods, understanding the chemical effects and phase stability in the Ti-Al system in the presence of other constituents will expedite developmental studies. Unfortunately, thermochemical and multiphase stability information related to the Ti-Al system is lacking. Only limited binary and ternary phase diagrams related to the Ti-Al system are available. When a multicomponent phase diagram of the real system is unavailable, the next best thing is to calculate the phase field of interest based on known thermodynamic information. Furthermore, the binary of the major constituents, Ti-Al in this case, forms the basis by which extrapolation into a multicomponent phase field is performed.

Until the late 1980s, Murray's Ti-Al phase diagram[13] was accepted in the material community (see Figure 6). Recent solidification experiments identified the existence of a high temperature α phase field not accounted for in Murray's phase diagram.[14] The experimental data raises uncertainties over the validity of Murray's Ti-Al phase diagram. This discrepancy is of significant importance since it occurs near the region where commercial γ-Ti-Al base alloys are being developed. Resolving this inconsistency is crucial in predicting synergistic effects with additional alloying elements. The purpose of this review is to consider recent developments in the determination of the Ti-Al phase diagram. A brief historical perspective in the development of the Ti-Al diagram is first presented. Due to special interest at MTL in XD™ Titanium Aluminide composites with near Ti-50 at.% Al compositions, a critical review with the emphasis on the near γ phase field will follow to determine reliability of the phase diagrams in dispute.

The Ti-Al System - A Historical Perspective of the Titanium - Rich End

The first complete Ti-Al phase diagram was reported by Ogden, et al.[15] in 1952. Ogden, et al. constructed the phase diagram with his experimental data from 0 at.% to 65 at.% Al in conjunction with results from Hansen[16] (1936) and Fink, et al.[17] (1931) for the 65 wt.% to 100 wt.% Al region (see Figure 1). From 30 at.% to 60 at.% Al, Ogden, et al.'s Ti-Al phase diagram showed two extrapolated peritectic reactions: $L + \beta \rightarrow \alpha$ at 1620°C and

$L + \alpha \rightarrow \gamma$ at 1480°C. An alternative phase diagram was proposed by Bumps, et al.[18] (1952) using experimental results from 0 at.% to 75 at.% Al (see Figure 2). Bumps, et al. concluded the existence of one peritectic reaction by extrapolation between 30 at.% to 60 at.% Al composition: $L + \beta \rightarrow \gamma$ at 1460°C. Within this region, a peritectoid determined experimentally, $\gamma + \beta \rightarrow \alpha$ at 1240°C was presented by Bumps, et al. and not accounted for in Ogden, et al.'s phase diagram. A short time later in 1956, Sagel, et al.[19] identified the $\alpha 2$ phase and the face-centered tetragonal ε phase (see Figure 3). The ε phase is commonly referred to as the gamma phase (γ Ti-Al). In 1961, Ence-Margolin[20] also reported the $\alpha 2$ phase (γ in Ence-Margolin's notation) experimentally. Ence-Margolin extrapolated their results and showed two peritectic reactions 30 at.% to 55 at.% Al: $L + \beta \rightarrow \delta$ (Ti_2Al) at 1460°C and $L + \delta$ (Ti_2Al) $\rightarrow \varepsilon$ (γ Ti-Al) at 1440°C. Subsequent studies including Crossley[21] in 1965 and Blackburn[22] in 1967 focussed on determining the $\alpha/(\alpha + \alpha 2)$ and the $(\alpha + \alpha 2)/\alpha 2$ boundaries (see Figure 4).

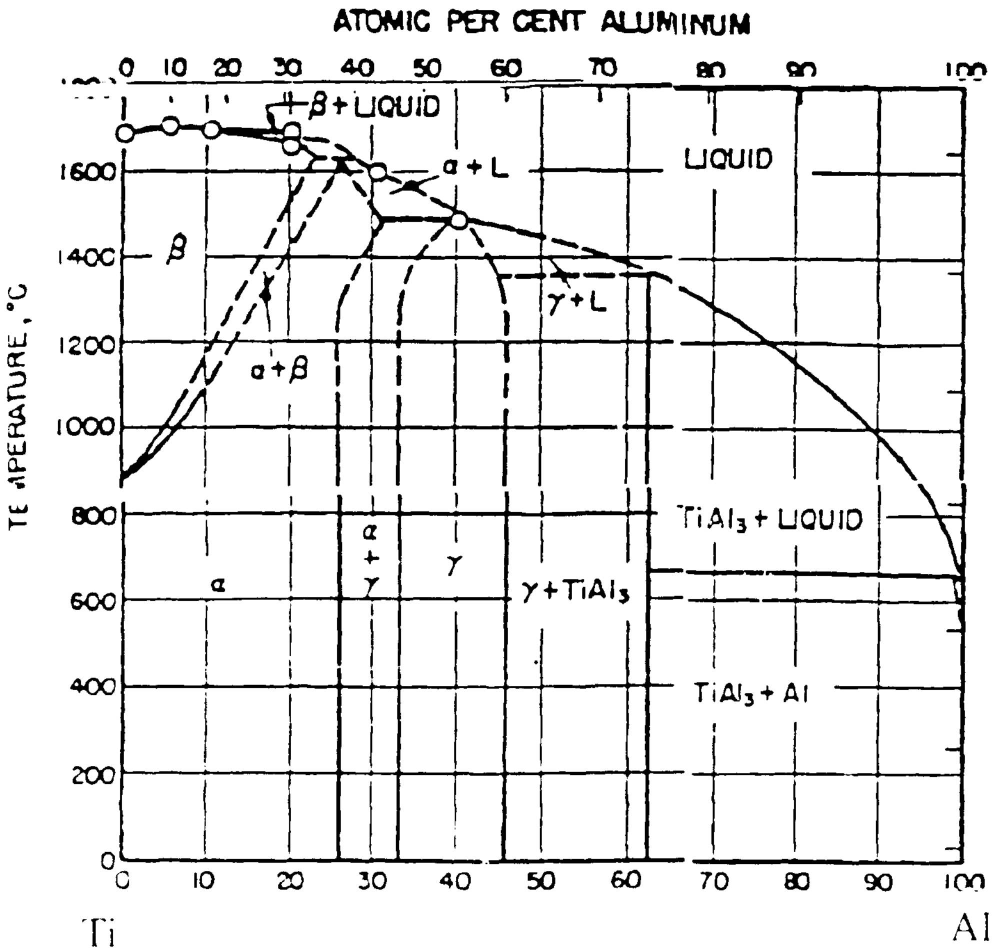

Figure 1. Binary phase diagram of Ti-Al - Ogden, et al.[15]

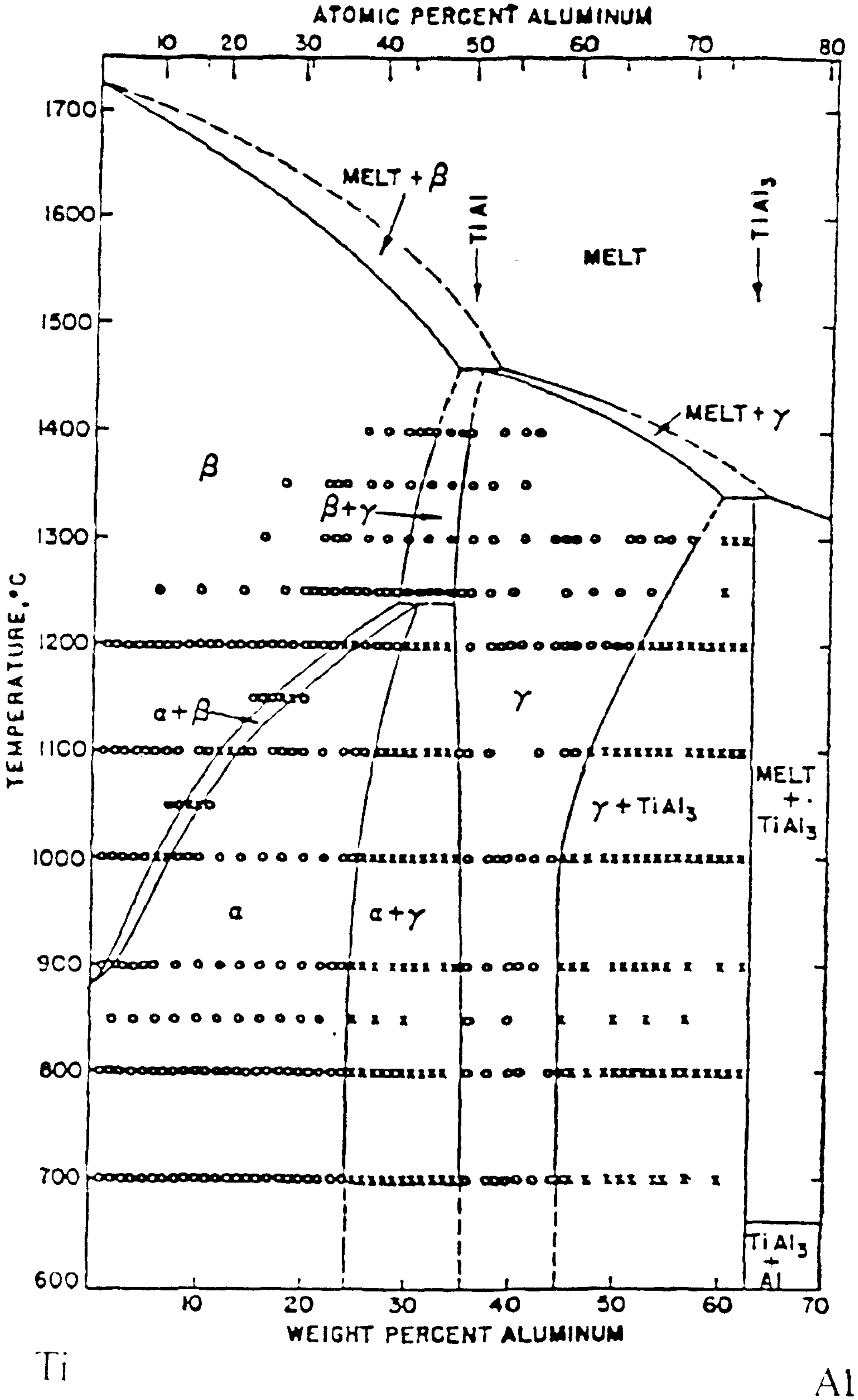

Figure 2. Binary phase diagram of Ti-Al - Bump, et al.[18]

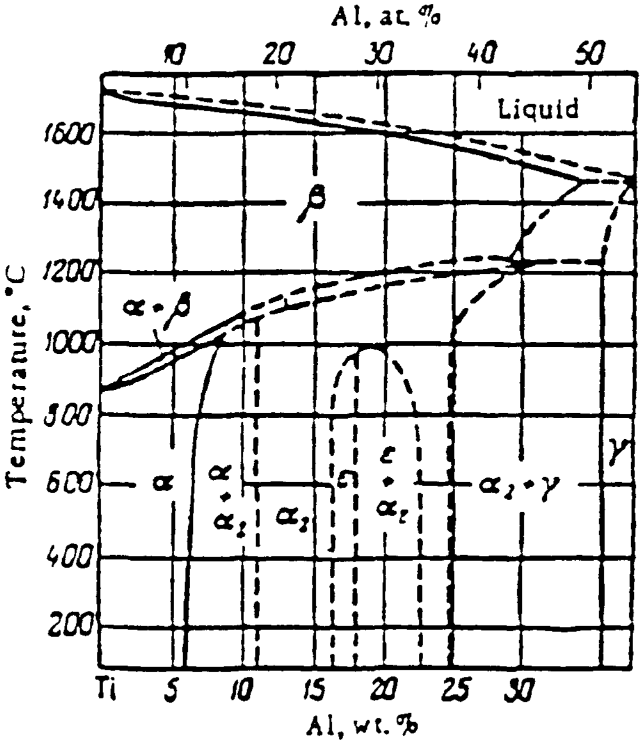

Figure 3. Binary phase diagram of Ti-Al - Sagel, et al.[19]

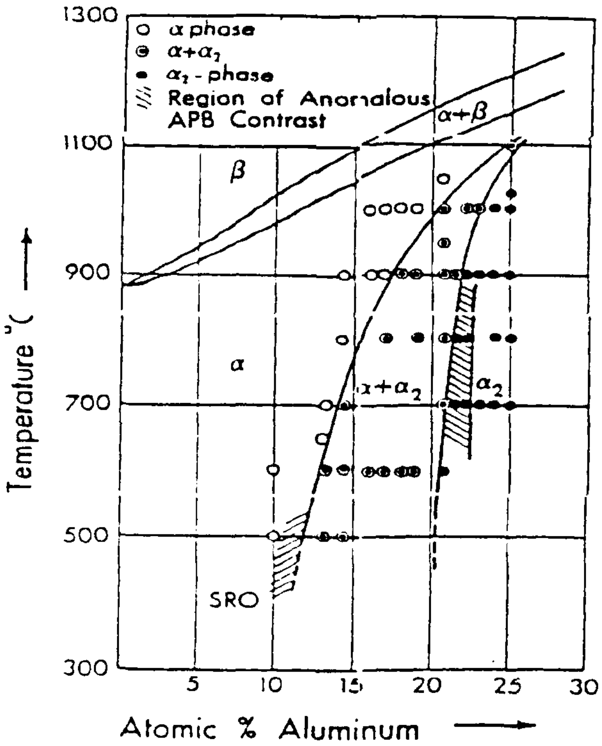

Figure 4. Binary phase diagram of Ti-Al - Blackburn, et al.[22]

The first calculated Ti-Al phase diagram was presented by Kaufman[23] in 1978. The calculated phase diagram is based on thermochemical data. Kaufman's Ti-Al phase diagram showed a high temperature eutectic ($L \rightarrow \beta + \gamma$) at 1525°C and a peritectoid ($\alpha 2 + \beta \rightarrow \alpha$) at 1150°C. The eutectic reaction did not agree with any previous studies. In 1979, Collings[24] reported heat treatment studies based on room temperature magnetic susceptibility measurements in determining the positions of the $\alpha 2/(\alpha 2 + \gamma)$ and $(\alpha 2 + \gamma)/\gamma$ phase boundaries. An estimate of 1315°C was made for the temperature of the horizontal $(\beta + \gamma)/(\gamma + \alpha)$ transus. The magnetic work did not distinguish between $\alpha + \gamma$ and $\alpha 2 + \gamma$ (see Figure 5). A more recent assessment of experimental data in calculating the Ti-Al system was presented by Murray[25,26] (see Figure 6). Murray's phase diagram was characteristically similar to Bumps, et al.'s[18] phase diagram showing only one peritectic ($\beta + L \rightarrow \gamma$) at 1500°C between 30 at.% and 50 at.% Al. A pertectoid reaction, $\beta + \gamma \rightarrow \alpha$ at 1285°C and a eutectic reaction $\alpha \rightarrow \alpha 2 + \gamma$ at 1125°C were evident from Murray's phase diagram. A short time later, solidification studies on near Ti-50 at.% Al by Graves, et al.,[27] Valencia, et al.,[14] McCullough, et al.,[28] Levi et al.,[29] and Oliver et al.[30] suggested this phase diagram be revised to include a stable (α + L) field and a second peritectic reaction $L + \alpha \rightarrow \gamma$. Shull, et al.[31] also reported a stable high temperature α field between the β and the γ phase fields. Based on previously assessed data,[25] Murray[13] recalculated the entire Ti-Al phase diagram retaining the single high temperature peritectic (see Figure 6) to explain rapid solidification microstructures. With additional experimental data from Mishurda, et al,[32] Chang, et al.[33] recalculated the Ti-Al phase diagram including the two peritectic reactions at the higher temperature (see Figure 7). More recently, Kim, et al.[34] published a Ti-Al phase diagram focussed between 30 at.% and 55 at.% Al (see Figure 8). General features of Kim's phase diagram[34] is in agreement with Chang's[33] phase diagram.

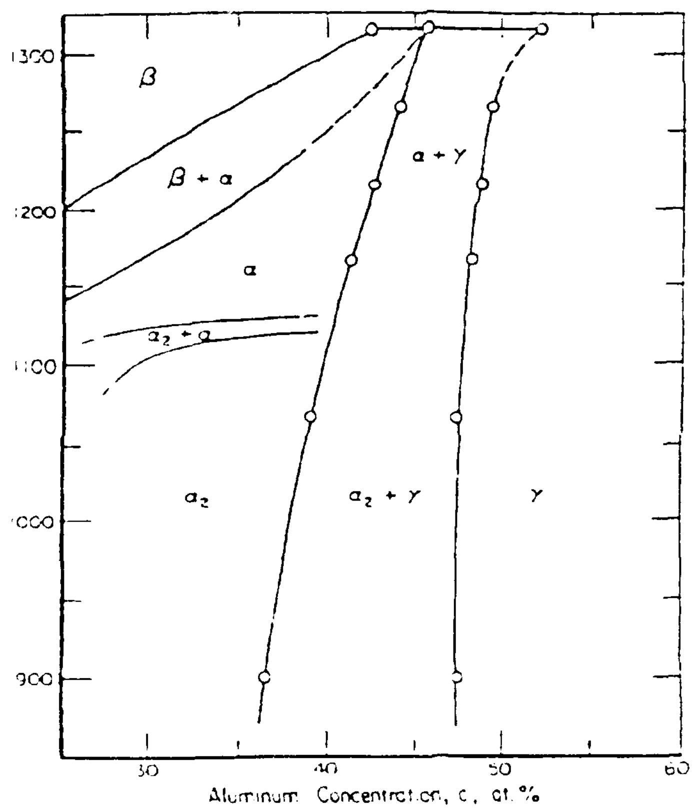

Figure 5. Binary phase diagram of Ti-Al - Collings[24] (Temperature in °C).

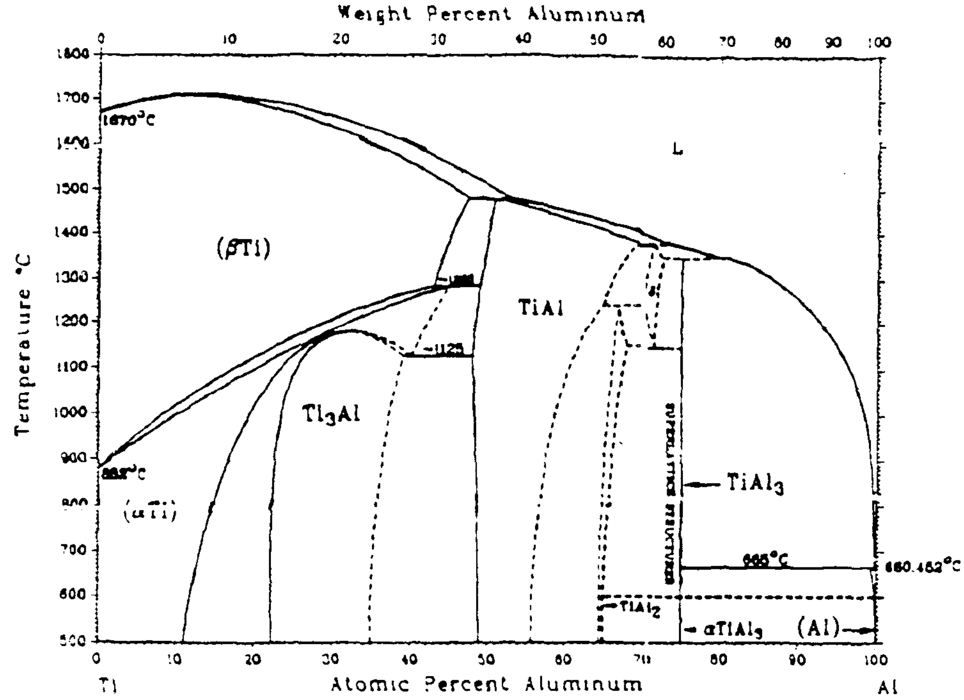

Figure 6. Binary phase diagram of Ti-Al - Murray.[25]

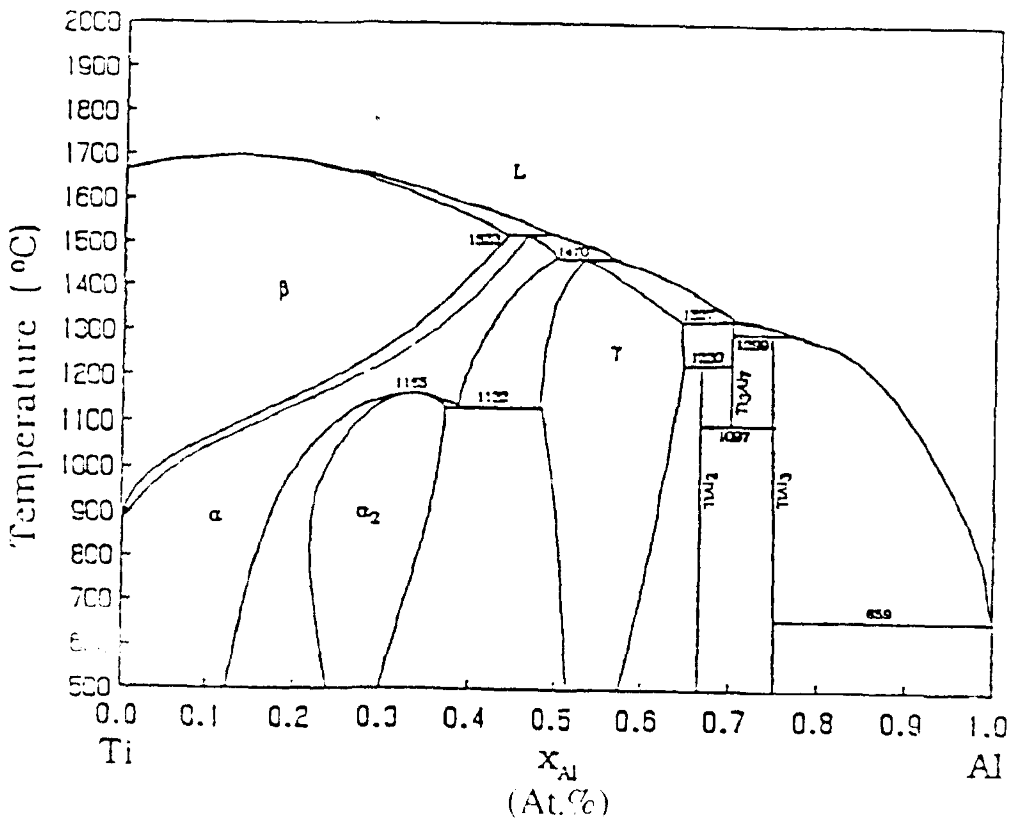

Figure 7. Binary phase diagram of Ti-Al - Chang, et al.[33]

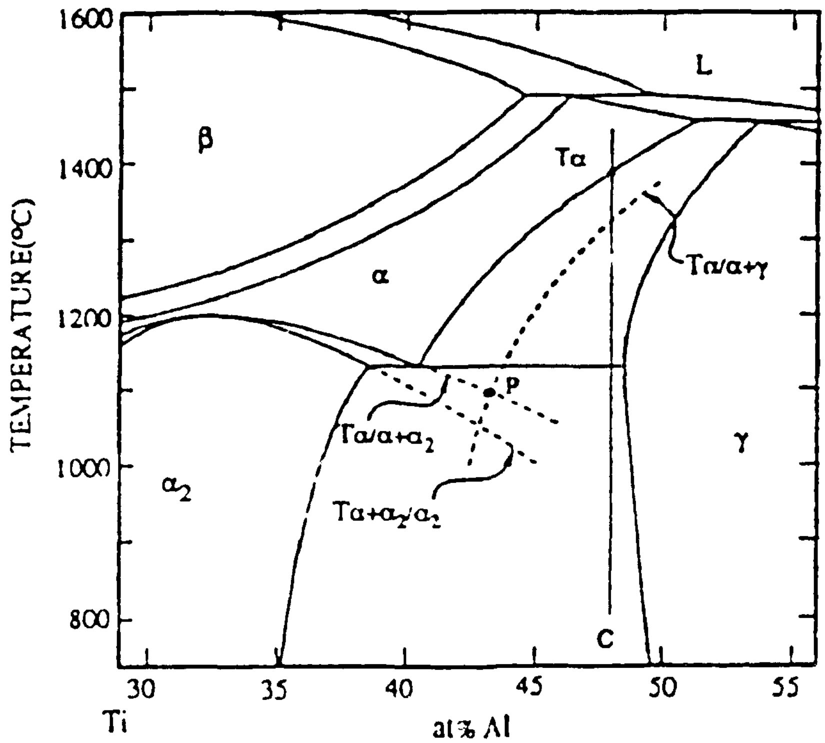

Figure 8. Binary phase diagram of Ti-Al - Kim.[34]

In summary, there are two versions of the Ti-Al phase diagrams which differ by whether there is one[13,18,24,25,26] or whether there are two[14,15,20,28,29] peritectic reactions for the region near 50 at.% Al between $\alpha 2$ and γ in the high temperature (1500°C) range (see Figure 9). Recent experimental and calculated results by Huang, et al.,[35] Mishurda, et al.,[32] Oliver, et al.,[30] Chang,[33] and Kim[34] supported the two peritectic reactions. The region of controversy near Ti-50 at.% Al is of great importance to the development of γ Ti-Al base alloys. Whether there is a high temperature α field, consistent with two peritectic reactions, or a β field, consistent with a single peritectic reaction, will determine whether an α or a β stabilizing element be added to alter the ternary microstructure. By critically reviewing issues underlining this dispute, an attempt will be made to determine which is the more accurate phase diagram· one with single peritectic (β + L → γ) calculated by Murray, or one with two peritectic (β + L → α) and (α + L → γ) calculated by Chang. Since details of Kim's analysis have not been published, only Murray's and Chang's phase diagrams will be discussed.

Near Stoichiometric Ti-Al Phase Field - A Critical Review

In Murray's[25] calculations, empirical Gibbs energy models were recast in terms of the Bragg-Williams[36] (B-W) approximation for order/disorder transitions. The sublattice model[37] represented the Gibbs energy for the bcc/B2, hcp/DO_{19}, and fcc/$L1_2$ order/disorder transformation. Least square optimization of thermochemical data was performed according to the programs of Lukas.[38] The linear combination of coefficients for this program was reexpressed in terms of coefficients used in the more general sublattice models.[39,40] Murray noted that a four sublattice model was needed to fit data for the $L1_0$ phase. Near the phase fields between 35 at.% to 50 at.% Al, Murray concluded that the calculated phase diagram was in good agreement with experimental data of Ogden, et al.,[15] Bumps, et al.,[18] Kornilov, et al.,[41] Ence and Margolin,[21] Collings,[24] and Ouchi, et al.[42] Murray's Ti-Al phase diagram shows a single peritectic (β + L $\rightarrow$ γ) at high temperatures.

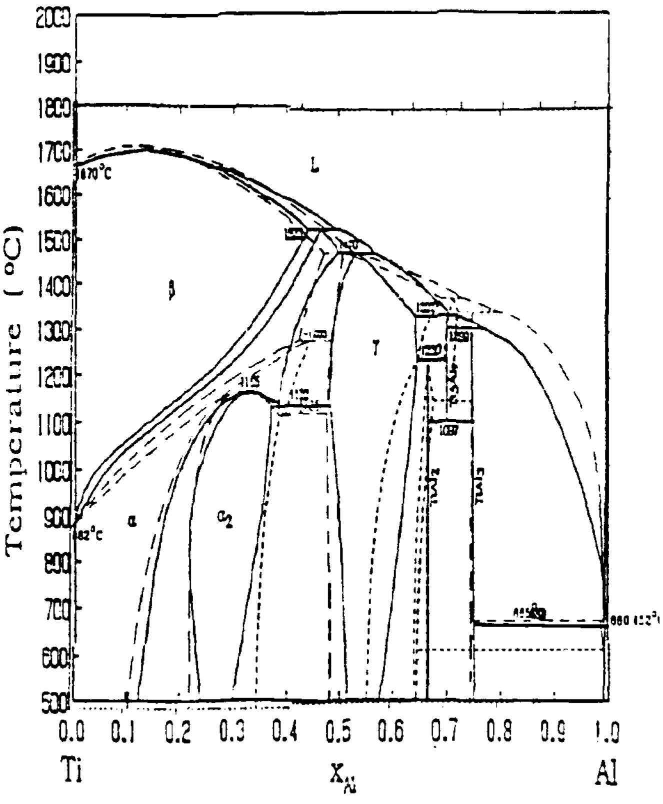

Figure 9. Overlapping of Binary phase diagram of Ti-Als by Murry and Chang.

In Chang's[33] calculation, a quasi-sub-subregular solution model[43] is used to describe the thermodynamic properties of the liquid phase and the solution phases exhibiting the hcp, bcc, and fcc structures. In the Gibbs calculations for γ and $\alpha 2$ phases, Orr's[44] extension of Wagner and Schottky's[45] substitutional disordering model for near stoichiometric composition was applied. The following assumptions were made:

- The interaction energies and thermal entropies are independent of composition
- Random mixing of atoms is assumed within their respective sublattices

The assumptions are similar to that of a regular solution applied to a sublattice mode. For the γ phase, the equations derived by Gyuk, Liang, and Chang[46,47] were used. For the $\alpha 2$ phase, the equations derived by Gyuk, Liang, and Chang[48] for the $L1_2$ phases were applied to the DO_{19} $\alpha 2$ phase. The assumption is that only the nearest neighbor interaction was considered. Since the first nearest neighbor arrangement of atoms of the DO_{19} structure is similar to that in the $L1_2$ structure, the Gibbs formalism derived for the $L1_2$ phase is applicable to the DO_{19} phase. For the γ phase, first and second nearest neighbor interactions were accounted. In Chang's[33] paper, experimental data from Mirshurda[32] at University of Wisconsin (UW)-Madison and coworkers of Levi and Mehrabian[14,28,29] at University of California

(UC)-Santa Barbara were utilized in formulating the phase diagram calculation. It was Graves[27] who first reported the high temperature α phase at UW-Madison in a rapid solidification experiment. Valencia, et al.,[14] McCullough, et al.,[28] and Levi, et al.[29] at UC-Santa Barbara performed other solidification experiments and suggested that the Ti-Al phase diagram should include a stable (α + L) field and a second peritectic reaction L + $\alpha \rightarrow \gamma$. Chang's calculated phase diagram reflects the recommendations from the research group at UC-Santa Barbara.

Modeling of a phase diagram is most useful in guiding extrapolations into multicomponent phase fields where experimental data are unavailable. Confirmation of a model in the binary system provides confidence in applying the formulation for a multicomponent system. It is typically impossible and unreasonable to expect a single mathematical model that is valid throughout the entire composition range and yet agree 100% with experimental data. Judgement is required in providing numerical adjustment to formulations used for estimating the best fit of available data within the confines of experimental error. This is done with some knowledge and intuition of qualitative effects due to alloying, presence of impurities, and existence of stable phases.

In Murray's study, it is not unreasonable to assume that the Ti-Al phase diagram was calculated with formulations best adjusted to fit the experimental data sited. Bumps, et al.[18] reported experimental results leading toward a single peritectic reaction. Ence and Margolin[20] reported experimental results that will extrapolate into two peritectic reactions. The phase and structural identification by both groups of researchers were later proven to be in error due to limited vacuum and high temperature X-ray capabilities during the 50s and early 60s. It was difficult and practically impossible to distinguish α, $\alpha 2$, and β at high temperatures. A vacuum system was limited to no better than 10^{-4} torr. Interstitial elements such as oxygen and nitrogen are alpha stabilizers. Heat treatments were performed for short durations ($\approx$10 minutes[18]) to avoid oxygen contamination. Results from heat treatment of titanium-aluminides performed at the U.S. Army Materials Technology Laboratory (MTL) under vacuum near 10^{-6} torr showed the formation of an alpha case on the specimen.[49] Impurity concentration was not reported after thermomechanical processing in producing the aluminides in any of the early reports. Furthermore, if a good vacuum was achieved, vapor pressure of aluminum would be high. Evaporation of aluminum is evident in any contained heat treating apparatus. It is questionable whether equilibrium condition was achieved when these experiments were performed. Also, when Murray made the phase diagram calculation, there was no experimental report in support of a high temperature α phase field. Consequently, the calculation made by Murray assured consistency of a single peritectic reaction and general agreement with known experimental data of Ogden, et al.,[15] Bumps, et al.,[18] Kornilov, et al.,[41] Ence and Margolin,[20] Collings,[24] and Ouchi, et al.[42]

A similar strategy was taken by Chang in the calculation of the Ti-Al phase diagram. However, Chang had access to recent experimental results from the UW-Madison and UC-Santa Barbara research groups. The solidification experiments were performed with specimens with less than 1000 ppm oxygen. The high temperature α phase was identified with electron diffraction studies. The ultra-fine resolution capability of electron microscopy when compared with X-ray, allows accurate studies of local equilibrium in the experiments. This form of analytical technique was not available in the early 1950s. The recent solidification studies were also in agreement with solidification experiments of Huang, et al.[35] at General Electric Corporate Research and Development Center. Consequently, Chang's calculation of the Ti-Al phase diagram is consistent with experimental results suggesting the existence of the two high temperature peritectic reactions.

It is well accepted by most researchers in the field of titanium-aluminides that the Ti-Al phase diagram should have two peritectic reactions, as presented by Chang.[50] Murray's diagram is in better agreement with older experimental data that indicate the existence of a single peritectic reaction (β + L $\rightarrow$ γ). As previously mentioned, the cleanliness of the specimens and experimental techniques used in the earlier works are questionable. One should also note that the vapor pressure of aluminum is relatively high at the higher temperature. Vacuum heat treatment of titanium-aluminide will leave a residue of aluminum on the furnace wall. Loss of aluminum will push the composition toward the titanium rich region corresponding to the high temperature β phase field since Al is an α stabilizer. Oxygen contamination will cause the formation of an α case since oxygen is an α stabilizer. In any case, many of the early experimental studies concluded from high temperature X-ray diffraction analysis of small specimens under vacuum may be in error. Furthermore, there is no real conclusion whether application of the sublattice model is any better or worse than models presented by Chang. The energy difference in determining whether there is one or two peritectic reactions is well within extrapolation, curve fitting, and experimental error.[51] In terms of the accuracy in applying the phase diagram, the error is difficult to assess without experimental data. One must also account for today's limitation in chemical analysis. Results on titanium-aluminide chemical analysis from certified analytical laboratories will vary ± 1 at.% in Al.[52] The chemical analysis error corresponds to an approximate difference of 100°C along the high temperature $\alpha/(\alpha + \gamma)$ boundary of both Murray's and Chang's phase diagram. A recent heat treatment study of Ti-48AL showed high temperature α-transus temperature below 1360°C.[53] The α-transus temperature at that composition is approximately 1420°C according to Chang's diagram. The specimens used in this heat treatment study have additions of boron. Whether the presence of boron can lower the α-transus by 100°C is being studied at Worcester Polytechnic Institute (WPI) and at MTL. Users of phase diagrams ought to be sensitive to the potential error associated with the use of real alloys and applicability of model in an extrapolated region.

SUMMARY

The Ti-Al phase diagram was critically reviewed. Until the late 1980s, Murray's Ti-Al phase diagram was accepted by the materials community. Recently, the accuracy of this diagram has come under dispute stemming from solidification experimental results which indicate that a high temperature α phase field is consistent with two high temperature peritectic reactions occurs (β + L $\rightarrow$ α; α + L $\rightarrow$ γ). This was not accounted for in Murray's phase diagram in which only one peritectic reaction was stated (β + $\rightarrow$ γ). Chang recalculated the Ti-Al phase diagram with the two proposed peritectic reactions. The different models used by Murray and Chang in their calculations served as an educated means by which the extrapolations and interpolations are performed in determining the phase boundaries. The results obtained by Murray and Chang provide a good example of how selection of differing models can yield significantly different phase diagrams. Both investigators relied heavily on experimental data in applying the model; the accuracy of their respective phase diagrams is dependent on the reliability of the experimental data. Chang's phase diagram is consistent with well accepted experimental results and is currently the accepted phase diagram in the titanium-aluminide community. Still, one must bear in mind the limitations in the interpretation of calculated phase diagrams, especially when working with *real* alloys. Recent experimental work at MTL showed that the presence of small amounts of impurities change the phase boundary by close to 100°C.

BIBLIOGRAPHY FOR THE Ti-Al PHASE DIAGRAM

Year	Authorship	Temp./Range (°C)	Composition (at.% Al)	Techniques
Aluminum-Rich				
1907	Manchot & Richter[54]		$Ti\text{-}Al_3$ (75 at.%)	
1923†	Erkelenz[55]		$Ti\text{-}Al_3$ (75 at.%)	
1926†	Manchot & Leber[56]		$Ti\text{-}Al_3$ (75 at.%)	
1931	Fink, et al.[17]		L + $Ti\text{-}Al_3$ (75 at.%) Al	
1934	Bohner[57]			
1936	Hansen[16]		$Ti\text{-}Al_3$ (51.2 at.%)	
1939	Brauer[58]			
1940	Nishimura, et al.[59]			
1943	Mondolfo[60]			
1943	Hanemann & Schrader[61]			
1946	Bückle[62]			
1948	Fink & Willey[63]		$Ti\text{-}Al_3$ (75 at.%)	
1949	Fink[64]	600-950	95-100 at.%	
1949	Hofmann[65]			
1950	Schubert[66]			
1952	Falkenhagen & Hofmann[67]			
1952*	Rostoker[68]			
1955	McQuillan[69]			
1958	Saulnier & Croutzeilles[70]			
1959	Saulnier & Croutzeilles[71]			
1961	Goldak, et al.[72]			
1961	Grum-Gvzhimailo, et al.[73]			
1964	Schubert, et al.[74]		$Ti\text{-}Al_2$, δ, $\alpha\text{-}Ti\text{-}Al_3$	
1964	Tavadze[75]		$Ti_9\text{-}Al$ & $Ti_2\text{-}Al$	
1965	Raman, et al.[76]		$Ti\text{-}Al_2$, δ, $\alpha\text{-}Ti\text{-}Al_3$ 60 at.% to 85 at.%	

Year	Authorship	Temp./Range (^{o}C)	Composition (at.% Al)	Techniques
1972	Maxwell & Hellawell[77]		L + Ti-Al_3→Al	
1973†	Loo & Rieck[78]		$\alpha/\zeta(\alpha2)$/K(γ-Ti-Al)/Ti-Al_2/ Ti_2-Al_5/θ-Ti-Al_3	
1974	Cisse, et al.[79]		L + Ti-Al_3 (75 at.%)→Al	
1974	Kerr, et al.[80]			
1974†	Heckler[81]	Solubility limit of Ti in Al (700°C to 1000°C)		
1978†	Shibata, et al.[82]		L + Ti-Al_3 →Al	
Titanium - Rich				
1950	Brown[83]			
1951*†	Ogden, et al.[15]	20-1100	0-64	O,X,T
1952*†	Bumps, et al.[18]	700-1400	0-75	O,X,HV
1952	Duwez & Taylor[84]	750		X
		Identified structure of Ti-Al		
1952	Gruhl[85]			
1954	Elliott & Rostoker[86]			
1954†	McQuillan[87]	880-970	0-12.6	
1955	Kubaschewski and Dench[88]			
1956†	Kornilov, et al.[41]	700-1200	0-100	O,X,HV,T,C
1956	Sagel, et al.[19]	550-1050	5-49	E,M,O,X
1956	Clark & Terry[89]			
1957	Ence and Margolin[90]			
1957	Crossley & Carew[91]			
1957	Anderko, et al.[92]			
1958*	Hansen[93]			
1960†	Sato and Huang[94]	450-1350	0-63	E,O,X
1961*†	Ence and Margolin[20]	800-1450	0-48	O,X
		Included Ti_2-Al & Ti_3-Al		

Year	Authorship	Temp./Range (^{o}C)	Composition (at.% Al)	Techniques
1961	Yao[95]	400-1100	5-38	M
1962*†	Clark, et al.[96]	550-1200	0-38	O,E,X
1965*	Elliott[97]			
1965	Kornilov, et al.[98]	550-1200	5-23	E,HV,T,D,X
1966†	Tsujimoto & Adachi[99]		peritectoid temp. at	$1100^{o}C$
1966*	Crossley[21]	550-1100	7-35	O,EM,X, DTA,E,D
1967†	Tsujimoto & Adachi[100]			α/β boundary
1967*†	Blackburn[22]	500-1100	7-35	EM
1970†	Jepson, et al.[101]			α/βboundary
1970†	Blackburn[102]	1025-1225	27-45	EM
1970†	Lutjering & Weissman[103]		Ti_3-Al/α	
1971†	Samolhval, et al.[104]		Ti_3-Al/α	
1973	Willey, et al.[105]			
1973	Hultgren, et al.[106]			
1973*	Margolin[107]			
1973†	Namboodhiri[108]		Ti_3-Al/α	
1976†	Zelenkov & Osokin[109]		Ti_3-Al/α	
1976†	Kornilov, et al.[110]		α/β boundary	
1977†	Sastry & Lipsitt[111]		Ti_3-Al	
1977†	Baggerly[112]		$\alpha/\alpha2$	
1978*	Kaufman[23]			Calculated
1978*	Moffatt[113]			
1979†	Mukhopadhyay[114]		$\alpha/\alpha2$	
1979*†	Collings[24]	900-1365	30-57	M
1980*	Banerjee, et al.[115]			
1980†	Ouchi, et al.[42]		α/β boundary	
1981*	Swartzendrulser, et al.[116]			

Year	Authorship	Temp./Range (^oC)	Composition (at.% Al)	Techniques
1983*	Liang[117]			
1984	Shull, et al.[31]		$\alpha/\alpha2$	
1985*	Murray[25,26]			
1987*	Graves, et al.[27]		50	
1987*	Valencia, et al.[14]		50	
1987	Levi, et al.[29]			
1988*	Murray[13]	500-1700	0-100	Calculated
1988*	McCullough, et al.[28]	25-1450	50	X
1989*	Mishurda, et al.[32]	25-1600	44-50	DTA,O, Calculated
1989*	McCullough, et al.[118]	25-1470	40-55	EM,X
1989*	Huang & Siemers[119]	1250-1475	46-65	O,D
1989*	Huang & Hall[35]			
1991*	Chang, et al.[33]			Calculated
1991*	Kim & Dimiduk[34]	750-1600	30-55	

*Reference reviewed

†Experimental data used to compare with calculations:

C	= Centrifugal Bend Test	HV	= Vickers Hardness
M	= Magnetic Susceptibility	D	= Dilatometry
DTA	= Differential Thermal Analysis	E	= Electrical Resistivity
EM	= Electron Microscopy	O	= Optical Metallography
T	= Thermal Analysis	X	= X-Ray Diffraction

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THE TITANIUM-ALUMINUM PHASE DIAGRAM - A REVIEW OF THE NEAR Ti-50 At.% Al PHASE FIELDS -
Ernest S. C. Chin and Ronald R. Biederman

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Technical Report MTL TR 92-47, July 1992, 21 pp-
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The understanding of the titanium-aluminum (Ti-Al) phase diagram is of great importance to the development of titanium-aluminide alloys and composites for high temperature applications. In this report, the Ti-Al phase diagram near 50 atomic percent (at.%) aluminum is critically reviewed. Murray's Ti-Al phase diagram has been well accepted by the materials community in the late 1980s. Recent results from solidification experiments point toward the existence of a high temperature α phase field consistent with two high temperature peritectic reactions ($\beta + L \rightarrow \alpha + L \rightarrow \gamma$) near 50 at.% aluminum. These reactions are not accounted for in Murray's Ti-Al phase diagram. Close evaluation of the past experimental techniques by which data were utilized in Murray's calculation of the Ti-Al phase diagram revealed areas of uncertainties. These uncertainties are primarily due to the limitation of analytical capabilities available at the time the experiments were performed.

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